



Application of Fourier-transform infrared spectroscopy for the determination of chloride and sulfate in wines



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ARTICLE INFO

Article history:

Received 21 October 2015

Received in revised form

24 November 2015

Accepted 25 November 2015

Available online 30 November 2015

Keywords:

FTIR

Chemometrics

PLS regression

Wine parameters

Ionic determination

ABSTRACT

Although a number of Fourier-transform infrared (FTIR) spectroscopy-based analytical methods for determination of control wine parameters have been reported over the past years, the potential of FTIR spectroscopy has not been fully explored in what concerns wine quality. In this work, FTIR spectroscopy and Partial Least Squares (PLS) regression, were combined for the development of a novel analytical method for chloride and sulfate determination in wines.

A careful selection and utilisation of different types of wine (to produce different matrices) was performed to ensure method's robustness. The developed FTIR spectroscopy-based method produced results with a very high accuracy especially for the determination of sulfate in wines ($R^2_{P,sulfate} = 0.98$, $RMSEP_{sulfate} = 0.11$ g/L and $RPD_{sulfate} = 6.3$). The developed method for the determination of chlorides in wine yielded enough accuracy and precision to allow semi-quantitative determinations ($R^2_{P,chloride} = 0.83$, $RMSEP_{chloride} = 0.18$ g/L and $RPD_{chloride} = 2.4$).

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1. Introduction

The quality of a wine can be achieved by a perfect balance of its analytical properties and consequent organoleptic characteristics. Therefore, the grape constitution and the vinification process result in a particular combination of components that will determine the wine character (Pizarro, Gonzalez-Saiz, Esteban-Diez, & Orío, 2011). Wine is mainly composed of water, ethanol and sugars, but also presents several other chemical elements (Cozzolino, Damberg, Janik, Cynkar, & Gishen, 2006). Among them are chloride and sulfate anions, which are as well, important indicators in the quality assessment of wine. Like other parameters, their concentration must obey legal requirements. Chloride anion is naturally present in wines, and its concentration is related to wine's geographical origin and corresponding geological and climatic conditions. The

frequently low chloride concentration in wines increases when they come from vineyards located near the coast. Moreover, high levels of chloride may also point out some fraudulent practices of filtration, stabilization (Lima & Rangel, 1989), clarification and organoleptic correction (Leske, Sas, Coulter, Stockley, & Lee, 1997) of wines.

The sulfate anion (SO_4^{2-}) is also part of the natural composition of wine, but several factors influence its concentration, like the soil composition where vines grow, the phytochemical treatments to which they were exposed and enological treatments. High levels of sulfate may increase wine astringency and protein haze formation, but it may also be an indicator of the addition of certain compounds like copper sulfate, ammonium sulfate and sulfuric acid. This addition aims to the improvement of wine quality, but in some cases is considered as fraudulent practices (Dugo, La Pera, Pellicanó, Di Bella, & D'Imperio, 2005; Tamasi, Pagni, Carapelli, Justice, & Cini, 2010).

Aiming to guarantee consumers' satisfaction as well as their health protection, several analytical procedures were developed for the assessment of wine safety and quality, in all stages of its

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production, (covering also the determination of chloride and sulfate anions in wine samples) (Dugo et al., 2005; Jun, Lima, & Montenegro, 1996; Mongay, Pastor, & Olmos, 1996). However, over the time has emerged the need to develop faster, automated and cost effective procedures, keeping at the same time a high level of reproducibility, precision and accuracy. Fourier-transform infrared (FTIR) spectroscopy appears as a possible solution complying with these requirements (Patz, Blieke, Ristow, & Dietrich, 2004). Apart from the benefits described above, this is a non-destructive technique, requiring very little sample preparation and avoiding the formation of toxic waste (de Villiers, Alberts, Tredoux, & Nieuwoudt, 2012).

Common drawbacks associated with infrared spectroscopy are particularly enhanced when applied to wine. The presence of water and ethanol, which dominate the absorption spectrum in the mid-infrared region, interferes with the determination of other important compounds. The chemical similarity of the major compounds present in wine, results in similar infrared absorption features (Bauer et al., 2008; Patz et al., 2004). Intensive calibration procedures combined with chemometric tools, such as Partial Least Squares (PLS) regression, provide the answers to overcome some of these problems.

Despite the large number of studies already performed, and even their implementation for routine analysis, the potential of FTIR spectroscopy has not been fully exhausted. Therefore the aim of this work was to evaluate FTIR suitability in the determination of chloride and sulfate concentrations in wine.

2. Materials and methods

2.1. Data set

A total of 45 different wine matrices were provided by the “Vinhos Verdes” Wine Commission in Portugal, to be the basis of the produced samples and experimental design (“Comissão de Viticultura da Região dos Vinhos Verdes (CVRVV, 2015). Available online at: <http://www.vinhoverde.pt/en/default.asp> (accessed 14 January 2015)”). In order to represent a wide diversity of wines and to increase the method's robustness, samples were selected to include several types (white, red, rosé, sparkling), and varieties of young wines (2012 and 2013 harvest) from different wineries, located in different Portuguese wine regions (Douro, Dão, Vinhos Verdes).

The low concentration and variability of the parameters, increases the difficulty of calibrations' development. Consequently, for chloride and sulfate determination, it was necessary to expand the original concentration ranges. For this purpose, the 45 representative wine matrices were divided in two sets of 20 and 25 samples and submitted to controlled fortifications of chloride and sulfate respectively. For each wine matrix, five concentration levels were selected and tested in order to respect the detection limits of the reference methodology and the maximum values allowed by law. From the experimental plan design, sets of 100 and 125 samples for chloride and sulfate parameters respectively, were produced. These sets encompass enough variability for the proper construction of predictive models and were simultaneously wide enough to include the limits established by legal regulations (1 g/L and 2 g/L for chloride and sulfate respectively) (“Diário da República - I Série-B. 2015. Available online at: http://www.ivv.min-agricultura.pt/np4/233?newsId=662&fileName=Portaria_334_94.pdf (accessed 14 January 2015)”).

The preparation of highly concentrated standard solutions of sodium chloride (Sigma–Aldrich, St. Louis MO, USA) and sulfuric acid (Sigma–Aldrich, St. Louis MO, USA), ensured a minimal addition of these solutions to the original samples, thus keeping the

original matrix effects unchanged.

Although commercial wines were used and sample pre-treatments were considered unnecessary, to avoid the possible presence of particles and to remove CO₂, all samples were filtered and degassed prior to measurements.

2.2. Reference analyses

The analytical reference results, used for sulfate and chloride calibrations, were obtained according to internal methodologies, based on continuous flow analyses and spectrophotometric detection with uncertainties of 17% and 15% respectively. The determination of sulfate is based in a colorimetric reaction, in which the colour intensity is directly proportional to the increase in the analyte. After dilution in a solution of barium chloride, the sulfate ions present in the sample, react with the barium leading to the formation of barium sulfate precipitate. The excess of barium resulting from the reaction is dialysed together with the colouring reagent. The colour decrease is measured on a UV/Vis spectrophotometer at 630 nm. Chloride determination is also based on a colorimetric reaction. However, in this case, the sample is diluted in a solution of mercury thiocyanate, which leads to the formation of mercury chloride and to the release of the thiocyanate ion. In the presence of the ferric ion, the thiocyanate forms a red complex, whose colour intensity is measured on a UV/Vis spectrophotometer at 490 nm. The number of samples and measurements, as well as some details are summarised in Table 1.

2.3. FTIR analyses

FTIR spectral acquisition was performed on previously filtered and degassed samples, using a Multispec IRTF UV/Visible (CETIM, France) spectrometer and an Avatar 370 (Thermo Nicolet Corporation, Madison, Wisconsin, USA) detector equipped with a Bacchus Acquisition/Quantification (CETIM, France) software.

Measurements were carried out in absorbance mode from 3050 to 1000 cm⁻¹, with a spectral resolution of 16 cm⁻¹, each spectrum being the average result of 22 scans.

Spectra were collected through the use of a CaF₂ cuvette, with an optical pathlength of 0.1 mm. Sampling was conducted with an auto-sampler, using about 10 ml of sample for a double measurement, including preflushing of the system, at 25 °C (adjusted by a Peltier system). Background measurements were taken against distilled water before every session of measurements. In order to avoid errors, due to chemical modifications, minimal periods of time elapsed between reference analyses and FTIR spectra acquisition.

2.4. Data processing

Spectra were collected between 3050 and 1000 cm⁻¹ (Fig. 1). Their visual analysis prompted the exclusion of the region between 1700 and 1570 cm⁻¹ due to signal saturation. In fact, other authors reported similar spectral behaviours near the above referred regions, due to strong water and ethanol absorptions (Fragoso, Acena, Guasch, Busto, & Mestres, 2011; Ozturk, Yucesoy, & Ozen, 2012; Pizarro et al., 2011; Regmi, Palma, & Barroso, 2012).

The resulting spectra (comprised between 1570–1000 and 3050–1700 cm⁻¹), were therefore subdivided into four spectral regions in agreement with the peaks and/or weak bands according to their disposition along the spectral wavelength. The four regions, as well as all their possible combinations, were evaluated for the construction of multivariate regression models. Several spectral pre-processing methods (such as standard normal variate (SNV) normalization, Savitzky–Golay first and second order derivatives,

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